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(54) Title: COSMETIC COMPOSITIONS

(57) Abstract: The invention relates to cosmetic compositions comprising a combination of non-emulsifying and emulsifying crosslinked siloxane elastomers.

COSMETIC COMPOSITIONS CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 60/217,211, filed July 10, 2000 and U.S. Provisional Application No. 60/276,998, filed March 19, 2001.

FIELD OF THE INVENTION

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The invention relates to cosmetic compositions comprising a combination of nonemulsifying and emulsifying crosslinked siloxane elastomers.

BACKGROUND OF THE INVENTION

Emollients including organic esters and hydrocarbons, especially petrolatum, have long been used medicinally as skin conditioning agents. These substances are second only to water as moisturizing ingredients of choice. They function primarily as an occlusive barrier. The water content of the outer layers of human skin stratum corneum is a controlling factor in the appearance of dry skin symptoms. When the stratum corneum contains an adequate amount of water within the range of ten to twenty percent, the skin remains flexible. However, when the water content falls below ten percent the stratum corneum often becomes brittle and rough and can exhibit scaling and cracking.

The stratum corneum receives its water from the deep layers of the epidermis by diffusion or when it is brought into direct contact with water. The diffusion process is controlled by the water content of the skin as well as the concentration gradient. In a very dry environment, the water loss from the external skin layers can be significant and often exceeds the rate of replacement by diffusion. An occlusive or semi-occlusive barrier substance placed on the surface of the skin acts to retard water loss to the environment. It also allows the skin surface to rehydrate via a diffusion mechanism.

While there are many effective and economical skin conditioning agents, they nevertheless suffer from certain disadvantages.

Often the emollient types are delivered as water-in-oil emulsions. It is difficult to attain the critical formula balance between oil and water phases to an extent sufficient to ensure long term storage stability. One part of this critical balance is the internal phase volume. A critical volume must be obtained to maximize the chemical and physical interactions, which produce and stabilize the system. If this critical volume is not balanced properly the product may suffer from viscosity change and eventual phase separation. Usually the optimum volume is quite large which limits the external phase volume size, and gives the system a draggy unfavorable slow

break attribute. This critical internal phase volume restriction can reduce functionality and add unfavorable feel characteristics.

New systems are needed to carry relatively high levels of aqueous based moisturizing ingredients (e.g. glycerin).

Accordingly, one aspect of the present invention is to provide cosmetic compositions, which provide improved skin-feel properties.

Another aspect of the present invention is to provide a skin treatment composition, which has stability against phase separation even under freeze/thaw cycling.

Still another aspect of the present invention is to provide a skin treatment composition, which achieves a smooth non-draggy rub-in upon initial application to the skin.

These and other aspects of the present invention will become more readily apparent from consideration of the following summary and detailed description.

SUMMARY OF THE INVENTION

The present invention relates to cosmetic compositions comprising:

- (i) from about 0.1% to about 15% of non-emulsifying crosslinked siloxane elastomer having a average particle size of at least 20 microns;
- (ii) from about 0.1% to about 15% of emulsifying cross-linked siloxane elastomer;
- (iii) from about 10 to about 80% of a solvent for the crosslinked siloxane elastomers;
- (iv) optionally, from 0 to about 50% of skin conditioning agent; and
- (v) from above about 0 to about 95% of water.

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Also disclosed herein are cosmetic compositions comprising:

- (i) from about 0.1% to about 15% of crosslinked siloxane elastomer having an average particle size less than 20 microns;
- (ii) from about 10 to about 80% of a solvent for the crosslinked siloxane elastomer;
- (iii) optionally, from 0 to about 50% of skin conditioning agent; and
- (iv) optionally, from above about 0 to about 95% of water wherein the composition contains at least about 1% air.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term "cosmetics" includes make-up, foundation, and skin care products. The term "make-up" refers to products that leave color on the face, including foundation, blacks and browns, i.e., mascara, concealers, eye liners, brow colors, eye shadows, blushers, lip colors, powders, solid emulsion compact, and so forth. "Skin care products" are those used to treat or care for, or somehow moisturize, improve, or clean the skin. Products

contemplated by the phrase "skin care products" include, but are not limited to, adhesives, bandages, toothpaste, anhydrous occlusive moisturizers, antiperspirants, deodorants, personal cleansing products, powder laundry detergent, fabric softener towels, occlusive drug delivery patches, nail polish, powders, tissues, wipes, hair conditioners-anhydrous, shaving creams and the like. The term "foundation" refers to liquid, creme, mousse, pancake, compact, concealer or like product created or reintroduced by cosmetic companies to even out the overall coloring of the skin. Foundation is manufactured to work better over moisturized and/or oiled skin. As used herein, "excess moisture" means an undesirable and/ or unhealthy level of bodily fluids deposited on human skin.

The term "ambient conditions" as used herein refers to surrounding conditions under about one atmosphere of pressure, at about 50% relative humidity, and at about 25°C., unless otherwise specified.

The term "yield point," as used herein is non-directional and refers to initial resistance to flow under applied stress; and is measured using Haake Controlled Stress Rheometer RS150 with a 35mm/4 deg. cone and plate.

As used herein the term "comprising" means that the composition can contain other ingredients which are compatible with the composition and which preferably do not substantially disrupt the compositions of the present invention. The term encompasses the terms "consisting of" and "consisting essentially of".

Unless otherwise indicated, all percentages and ratios used herein are by weight of the total composition. All weight percentages, unless otherwise indicated, are on an actives weight basis. All measurements made are at 25°C, unless otherwise designated.

Crosslinked Siloxane Elastomer

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An essential component of the present invention is a crosslinked organopolysiloxane elastomer. No specific restriction exists as to the type of curable organopolysiloxane composition, which can serve as the starting material for the crosslinked organopolysiloxane elastomer. Examples in this respect are addition reaction-curing organopolysiloxane compositions which cure under platinum metal catalysis by the addition reaction between SiH-containing diorganopolysiloxane and organopolysiloxane having silicon-bonded vinyl groups; condensation-curing organopolysiloxane compositions which cure in the presence of an organotin compound by a dehydrogenation reaction between hydroxyl-terminated diorganopolysiloxane and SiH-containing diorganopolysiloxane; condensation-curing organopolysiloxane compositions which cure in the presence of an organotin compound or a titanate ester, by a condensation

reaction between an hydroxyl-terminated diorganopolysiloxane and a hydrolyzable organosilane (this condensation reaction is exemplified by dehydration, alcohol-liberating, oxime-liberating, amine-liberating, amide-liberating, carboxyl-liberating, and ketone-liberating reactions); peroxide-curing organopolysiloxane compositions which thermally cure in the presence of an organoperoxide catalyst; and organopolysiloxane compositions which are cured by high-energy radiation, such as by gamma-rays, ultraviolet radiation, or electron beams.

Addition reaction-curing organopolysiloxane compositions are preferred for their rapid curing rates and excellent uniformity of curing. A particularly preferred addition reaction-curing organopolysiloxane composition is prepared from:

- (A) an organopolysiloxane having at least 2 lower alkenyl groups in each molecule;
- (B) an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule; and
 - (C) a platinum-type catalyst.

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With regard to the above, component (A) is the basic component of the silicone elastomer-generating organopolysiloxane, and curing proceeds by the addition reaction of this component with component (B) under catalysis by component (C). This component (A) must contain at least 2 silicon-bonded lower alkenyl groups in each molecule; an excellent cured product will not be obtained at fewer than two lower alkenyl groups because a network structure will not be formed. Said lower alkenyl groups are exemplified by vinyl, allyl, and propenyl. While the lower alkenyl groups can be present at any position in the molecule, their presence at the molecular terminals is preferred. The molecular structure of this component may be straight chain, branched straight chain, cyclic, or network, but a straight chain, possibly slightly branched, is preferred. The molecular weight of the component is not specifically restricted, and thus the viscosity may range from low viscosity liquids to very high viscosity gums. In order for the cured product to be obtained in the form of the rubbery elastomer, it is preferred that the viscosity These organopolysiloxanes are exemplified by at 25°C be at least 100 centistokes. methylvinylsiloxanes, methylvinylsiloxane-dimethylsiloxane copolymers, dimethylvinylsiloxydimethylsiloxanedimethylvinylsiloxy-terminated terminated dimethylpolysiloxanes, dimethylsiloxanemethylphenylsiloxane copolymers, dimethylvinylsiloxy-terminated diphenylsiloxane-methylvinylsiloxane copolymers, trimethylsiloxy-terminated dimethylsiloxanedimethylsiloxanetrimethylsiloxy-terminated methylvinylsiloxane copolymers, dimethylvinylsiloxy-terminated methylphenylsiloxane-methylvinylsiloxane copolymers,

methyl(3,3,3-trifluoropropyl) polysiloxanes, and dimethylvinylsiloxy-terminated dimethylsiloxane-methyl(3,3,-trifluoropropyl)siloxane copolymers.

Component (B) is an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule and is a crosslinker for component (A). Curing proceeds by the addition reaction of the silicon-bonded hydrogen atoms in this component with the lower alkenyl groups in component (A) under catalysis by component (C). This component (B) must contain at least 2 silicon-bonded hydrogen atoms in each molecule in order to function as a crosslinker. Furthermore, the sum of the number of alkenyl groups in each molecule of component (A) and the number of silicon-bonded hydrogen atoms in each molecule of component (B) is to be at least 5. Values below 5 should be avoided because a network structure is then essentially not formed.

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No specific restriction exists on the molecular structure of this component, and it may be any of straight chain, branch-containing straight chain, cyclic, etc. The molecular weight of this component is not specifically restricted, but it is preferred that the viscosity at 25°C be 1 to 50,000 centistokes in order to obtain good miscibility with component (A). It is preferred that this component be added in a quantity such that the molar ratio between the total quantity of silicon-bonded hydrogen atoms in the instant component and the total quantity of all lower alkenyl groups in component (A) falls within the range of 1.5:1 to 20:1. It is difficult to obtain good curing properties when this molar ratio falls below 0.5:1. When 20:1 is exceeded, there is a tendency for the hardness to increase to high levels when the cured product is heated. Furthermore, when an organosiloxane containing substantial alkenyl is supplementarily added for the purpose of; for example, reinforcement, it is preferred that a supplemental addition of the instant SiH-containing component be made in a quantity offsetting these alkenyl groups. This trimethylsiloxy-terminated exemplified by concretely component is trimethylsiloxy-terminated dimethylsiloxanemethylhydrogenpolysiloxanes, methylhydrogensiloxane copolymers, and dimethylsiloxane-methylhydrogen-siloxane cyclic copolymers.

Component (C) is a catalyst of the addition reaction of silicon-bonded hydrogen atoms and alkenyl groups, and is concretely exemplified by chloroplatinic acid, possibly dissolved in an alcohol or ketone and this solution optionally aged, chloroplatinic acid-olefin complexes, chloroplatinic acid-alkenylsiloxane complexes, chloroplatinic acid-diketone complexes, platinum black, and carrier-supported platinum.

This component is added preferably at 0.1 to 1,000 weight parts, and more preferably at 1 to 100 weight parts, as platinum-type metal proper per 1,000,000 weight parts of the total

quantity of components (A) plus (B). Other organic groups which may be bonded to silicon in the organopolysiloxane forming the basis for the above-described curable organopolysiloxane compositions are, for example, alkyl groups such as methyl, ethyl, propyl, butyl, and octyl; substituted alkyl groups such as 2-phenylethyl, 2-phenylpropyl, and 3,3,3-trifluoropropyl; aryl groups such as phenyl, tolyl, and xylyl; substituted aryl groups such as phenylethyl; and monovalent hydrocarbon groups substituted by, for example, the epoxy group, the carboxylate ester group, the mercapto group, etc.

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Examples of the production of the organopolysiloxane elastomer powder are as follows: an organopolysiloxane composition as described above (additional-curable, condensationcurable, or peroxide-curable) is mixed with water in the presence of a surfactant (nonionic, anionic, cationic, or amphoteric), and, after mixing to homogeneity in a homomixer, colloid mill, homogenizer, propeller mixer, etc., this is cured by discharge into hot water (temperature at least 50°C) and is then dried; the organopolysiloxane composition (addition-curable, condensationcurable, or peroxide-curable) is cured by spraying it directly into a heated current; the powder is obtained by curing a radiation-curable organopolysiloxane composition by spraying it under high energy radiation; the organopolysiloxane composition (addition-curable, condensation-curable, peroxide-curable) or high energy-curable organopolysiloxane composition is cured, the latter by high energy radiation, and the product is then pulverized using a known pulverizer such as, for example, a ball mill, atomizer, kneader, roll mill, etc., to thereby form the powder. Suitable organopolysiloxane elastomer powders include vinyl dimethicone/methicone silesquioxane crosspolymers like Shin-Etsu's KSP-100, KSP-101, KSP-102, KSP-103, KSP-104, KSP-105, hybrid silicone powders that contain a fluoroalkyl group like Shin-Etsu's KSP-200, and hybrid silicone powders that contain a phenyl group such as Shin-Etsu's KSP-300; and Dow Corning's DC 9506.

Preferred organopolysiloxane compositions are dimethicone/vinyl dimethicone crosspolymers. Such dimethicone/vinyl dimethicone crosspolymers are supplied by a variety of suppliers including Dow Corning (DC 9040 and DC 9041), General Electric (SFE 839), Shin Etsu (KSG-15, 16, 18 [dimethicone /phenyl vinyl dimethicone crosspolymer]), Grant Industries (Gransil™ line of materials), and lauryl dimethicone/vinyl dimethicone crosspolymers supplied by Shin Etsu (e.g., KSG-31, KSG-32, KSG-41, KSG-42, KSG-43, and KSG-44). Cross-linked organopolysiloxane elastomers useful in the present invention and processes for making them are further described in US Patent 4,970,252 to Sakuta et al., issued November13, 1990; US Patent 5,760,116 to Kilgour et al., issued June 2, 1998; US Patent 5,654,362 to Schulz, Jr. et al. issued

August 5, 1997; and Japanese Patent Application JP 61-18708, assigned to Pola Kasei Kogyo KK, each of which are herein incorporated by reference in its entirety.

The compositions of the present invention comprise a combination of emulsifying and non-emulsifying crosslinked organopolysiloxane elastomer. The term "non-emulsifying," as used herein, defines crosslinked organopolysiloxane elastomer from which polyoxyalkylene units are absent. The term "emulsifying," as used herein, means crosslinked organopolysiloxane elastomer having at least one polyoxyalkylene unit. Emulsifying crosslinked organopolysiloxane elastomer can notably be chosen from the crosslinked polymers described in US Patents 5,412,004 (issued 5/2/95); 5,837,793 (issued 11/17/98); and 5,811,487 (issued 9/22/98), all of which are herein incorporated by reference in their entirety.

Particularly useful emulsifying elastomers are polyoxyalkylene modified elastomers formed from divinyl compounds, particularly siloxane polymers with at least two free vinyl groups, reacting with Si-H linkages on a polysiloxane backbone. Preferably, the elastomers are dimethyl polysiloxanes crosslinked by Si-H sites on a molecularly spherical MQ resin.

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The non-emulsifying cross-linked organopolysiloxane elastomers of the present invention are preferably further processed by subjecting them to a high shear (approximately 5,000 psi) treatment in the presence of a solvent for the siloxane elastomer via a Sonolator at less than 10 passes. Sonolation achieves a resultant composition with elastomer average particle size ranging from at least 20 (or about 20) microns to about 200 microns, preferably from about 30 to about 150 microns, more preferably from 40 (or about 40) to about 95 microns and most preferably from about 50 microns to about 90 microns as measured by the Horiba LA-910 (described below). As used herein, the term "particle size" of the elastomer represents the elastomer particle size in its swelled state. By "swelled," as used herein, means that the elastomer particles have extended beyond their normal size and shape by virtue of their absorption of the solvent compound. Viscosity is best when ranging between above 20,000 (or above about 20,000) and about 6,000,000, preferably from about 25,000 to about 4,000,000, more preferably from about 30,000 to about 3,000,000, most preferably from about 40,000 to about 2,000,000, optimally about 60,000 to about 1,500,000 cps at 25°C as measured by a Brookfield LV Viscometer (size 4 bar, 60 rpm, 0.3 sec.).

Without being limited by theory, the present inventors believe that compositions incorporating non-emulsifying elastomer/solvent gels where the non-emulsifying cross-linked organopolysiloxane elastomer has an average particle size greater than 10 microns (or greater than about 10 microns) and/or viscosities greater than 20,000 cps provide films having improved

smoothness as well as improved uniformity and evenness of particle (e.g., pigments) distribution within the film (i.e., solid particles remain distributed within and throughout the film as opposed to such particles protruding from the film into and/or across the film/air interface).

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Preferably, the non-emulsifying cross-linked organopolysiloxane elastomers do not undergo recycled processing. Without being limited by theory, recycled processing produces broad particle size distributions comprising particles larger or smaller than that necessary to achieve the skin feel benefits of the present invention. Specifically, gel balls often result from silicone elastomer particles larger than 200 microns while elastomer particles smaller than 10 microns reduce skin feel and viscosity benefits. Such particle size distributions result from a failure to ensure that all of the elastomer particle materials experience the same shear throughout the process. Typically, with recycling, only a portion of the particles experience shear before these sheared particles are returned to the process starting point and combined with the remaining un-sheared particles. Similarly, the next cycle begins with only a portion of this particle mixture experiencing before the newly sheared mixture particles are returned to the process starting point and combined with the remaining un-sheared particle mixture. Importantly, even after considerable recycling, some of the particles never actually experience shear while others experience a high degree of shear. The result is a particle size range, which encompasses particles both larger and smaller than those necessary to achieve the present invention.

In contrast, discrete pass processing, as alluded to above, ensures that all the particles experience shear as well as the same amount of shear with each run or pass. More specifically, no run or pass is completed until all the particles have experienced the same shear force. Consequently, the particle size distribution is narrower than that produced by "recycling" with respect to specific particle sizes. This results in a better balance between gel ball formation and viscosity as well as skin feel and viscosity.

The non-emulsifying crosslinked organopolysiloxane elastomer is present in the compositions of the present invention at concentrations of from about 0.1 to about 15%, optimally from about 1 to about 10%, most preferably from about 3 to about 8% by weight.

The emulsifying crosslinked organopolysiloxane elastomer is present in the compositions of the present invention at concentrations of from about 0.1 to about 15%, optimally from about 1 to about 10%, most preferably from about 3 to about 8% by weight.

Solvent for the Non-emulsifying and Emulsifying Crosslinked Siloxane Elastomer

The compositions of the present invention comprise a solvent for the crosslinked organopolysiloxane elastomer described above. The solvent, when combined with the cross-

linked organopolysiloxane elastomer particles of the present invention, serves to suspend and swell the elastomer particles to provide an elastic, gel-like network or matrix. The solvent for the cross-linked siloxane elastomer is liquid under ambient conditions, and preferably has a low viscosity to provide for improved spreading on the skin.

Concentrations of the solvent in the cosmetic compositions of the present invention will vary primarily with the type and amount of solvent and the cross-linked siloxane elastomer employed. Preferred concentrations of the solvent are from about 10% to about 90%, preferably from about 20% to about 80%, more preferably from about 30% to about 70%, by weight of the composition.

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The solvent for the cross-linked siloxane elastomer comprises one or more liquid carriers suitable for topical application to human skin. These liquid carriers may be organic, silicone-containing or fluorine-containing, volatile or non-volatile, polar or non-polar, provided that the liquid carrier forms a solution or other homogenous liquid or liquid dispersion with the selected cross-linked siloxane elastomer at the selected siloxane elastomer concentration at a temperature of from about 28°C to about 250°C, preferably from about 28°C to about 100°C, preferably from about 28°C to about 78°C. The solvent for the cross-linked siloxane elastomer preferably has a solubility parameter of from about 3 to about 13 (cal/cm³)^{0.5}, more preferably from about 5 to about 11 (cal/cm³)^{0.5}, most preferably from about 5 to about 9 (cal/cm³)^{0.5}. Solubility parameters for the liquid carriers or other materials, and means for determining such parameters, are well known in the chemical arts. A description of solubility parameters and means for determining them are described by C. D. Vaughan, "Solubility Effects in Product, Package, Penetration and Preservation" 103 Cosmetics and Toiletries 47-69, October 1988; and C. D. Vaughan, "Using Solubility Parameters in Cosmetics Formulation", 36 J. Soc. Cosmetic Chemists 319-333, September/October, 1988, which articles are incorporated herein by reference.

The solvent preferably includes volatile, non-polar oils; non-volatile, relatively polar oils; non-volatile, non-polar oils; and non-volatile paraffinic hydrocarbon oils; each discussed more fully hereinafter. The term "non-volatile" as used herein refers to materials which exhibit a vapor pressure of no more than about 0.2 mm Hg at 25°C at one atmosphere and/or to materials that have a boiling point at one atmosphere of at least about 300°C. The term "volatile" as used herein refers to all materials that are not "non-volatile" as previously defined herein. The phrase "relatively polar" as used herein means more polar than another material in terms of solubility parameter; i.e., the higher the solubility parameter the more polar the liquid.

The term "non-polar" typically means that the material has a solubility parameter below about 6.5 (cal/cm³)^{0.5}.

1. Non-polar, Volatile Oils

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The non-polar, volatile oil tends to impart highly desirable aesthetic properties to the compositions of the present invention. Consequently, the non-polar, volatile oils are preferably utilized at a fairly high level. Non-polar, volatile oils particularly useful in the present invention are selected from the group consisting of silicone oils; hydrocarbons; and mixtures thereof. Such non-polar, volatile oils are disclosed, for example, in Cosmetics, Science, and Technology, Vol. 1, 27-104 edited by Balsam and Sagarin, 1972. The non-polar, volatile oils useful in the present invention may be either saturated or unsaturated, have an aliphatic character and be straight or branched chained or contain alicyclic or aromatic rings. Examples of preferred nonpolar, volatile hydrocarbons include polydecanes such as isododecane and isodecane (e.g., Permethyl-99A which is available from Presperse Inc.) and the C7 -C8 through C12 -C15 isoparaffins (such as the Isopar Series available from Exxon Chemicals). Non-polar, volatile liquid silicone oils are disclosed in U.S. Patent 4,781,917 issued to Luebbe et al. on Nov. 1, 1988, herein incorporated by reference in its entirety. Additionally, a description of various volatile silicones materials is found in Todd et al., "Volatile Silicone Fluids for Cosmetics", Cosmetics and Toiletries, 91:27-32 (1976), herein incorporated by reference in its entirety. Particularly preferred volatile silicone oils are selected from the group consisting of cyclic volatile silicones corresponding to the formula:

wherein n is from about 3 to about 7; and linear volatile silicones corresponding to the formula: (CH₃)₃ Si-O-[Si(CH₃)₂-O]_m -Si(CH₃)₃

wherein m is from about 1 to about 7. Linear volatile silicones generally have a viscosity of less than about 5 centistokes at 25°C., whereas the cyclic silicones have viscosities of less than about 10 centistokes at 25°C. Highly preferred examples of volatile silicone oils include cyclomethicones of varying viscosities, e.g., Dow Corning 200, Dow Corning 244, Dow Corning 245, Dow Corning 344, and Dow Corning 345, (commercially available from Dow Corning Corp.); SF-1204 and SF-1202 Silicone Fluids (commercially available from G.E. Silicones), GE

7207 and 7158 (commercially available from General Electric Co.); and SWS-03314 (commercially available from SWS Silicones Corp.).

2. Relatively Polar, Non-volatile oils

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The non-volatile oil is "relatively polar" as compared to the non-polar, volatile oil discussed above. Therefore, the non-volatile co-solvent is more polar (i.e., has a higher solubility parameter) than at least one of the non-polar, volatile oils. Relatively polar, nonvolatile oils potentially useful in the present invention are disclosed, for example, in Cosmetics, Science, and Technology, Vol. 1, 27-104 edited by Balsam and Sagarin, 1972; U.S. Patents 4,202,879 issued to Shelton on May 13, 1980; and 4,816,261 issued to Luebbe et al. on Mar. 28, 1989, all of which are herein incorporated by reference in their entirety. Relatively polar, nonvolatile oils useful in the present invention are preferably selected from the group consisting of silicone oils; hydrocarbon oils; fatty alcohols; fatty acids; esters of mono and dibasic carboxylic acids with mono and polyhydric alcohols; polyoxyethylenes; polyoxypropylenes; mixtures of polyoxyethylene and polyoxypropylene ethers of fatty alcohols; and mixtures thereof. The relatively polar, non-volatile co-solvents useful in the present invention may be either saturated or unsaturated, have an aliphatic character and be straight or branched chained or contain alicyclic or aromatic rings. More preferably, the relatively polar, non-volatile liquid co-solvent are selected from the group consisting of fatty alcohols having from about 12-26 carbon atoms; fatty acids having from about 12-26 carbon atoms; esters of monobasic carboxylic acids and alcohols having from about 14-30 carbon atoms; esters of dibasic carboxylic acids and alcohols having from about 10-30 carbon atoms; esters of polyhydric alcohols and carboxylic acids having from about 5-26 carbon atoms; ethoxylated, propoxylated, and mixtures of ethoxylated and propoxylated ethers of fatty alcohols with from about 12-26 carbon atoms and a degree of ethoxylation and propoxylation of below about 50; and mixtures thereof. More preferred are propoxylated ethers of C14 -C18 fatty alcohols having a degree of propoxylation below about 50, esters of C2 -C8 alcohols and C12-C26 carboxylic acids (e.g. ethyl myristate, isopropyl palmitate), esters of C12-C26 alcohols and benzoic acid (e.g. Finsolv TN supplied by Finetex), diesters of C2-C8 alcohols and adipic, sebacic, and phthalic acids (e.g., diisopropyl sebacate, diisopropyl adipate, di-n-butyl phthalate), polyhydric alcohol esters of C6 -C26 carboxylic acids (e.g., propylene glycol dicaprate/dicaprylate, propylene glycol isostearate); and mixtures thereof. Even more preferred are branched-chain aliphatic fatty alcohols having from about 12-26 carbon Even more preferred are isocetyl alcohol; octyldecanol, octyldodecanol and atoms. undecylpentadecanol; and most preferred is octyldodecanol. Such preferred aliphatic fatty

alcohols are particularly useful in combination with the volatile liquid silicone oils discussed herein to adjust the average solubility of the solvent.

3. Non-polar, Non-volatile oils

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In addition to the liquids discussed above, the solvent for the cross-linked siloxane elastomer may optionally include non-volatile, non-polar oils. Typical non-volatile, non-polar emollients are disclosed, for example, in Cosmetics, Science, and Technology, Vol. 1, 27-104 edited by Balsam and Sagarin, 1972; U.S. Patents 4,202,879 issued to Shelton on May 13, 1980; and 4,816,261 issued to Luebbe et al. on Mar. 28, 1989, both of which are herein incorporated by reference. The non-volatile oils useful in the present invention are essentially non-volatile polysiloxanes, paraffinic hydrocarbon oils, and mixtures thereof. The polysiloxanes useful in the present invention selected from the group consisting of polyalkylsiloxanes, polyarylsiloxanes, polyalkylarylsiloxanes, poly-ethersiloxane copolymers, and mixtures thereof. Examples of these include polydimethyl siloxanes having viscosities of from about 1 to about 100,000 centistokes at 25° C. Among the preferred non-volatile silicone emollients useful in the present compositions are the polydimethyl siloxanes having viscosities from about 2 to about 400 centistokes at 25°C. Such polyalkylsiloxanes include the Viscasil series (sold by General Electric Company) and the Dow Corning 200 series (sold by Dow Corning Corp.). Polyalkylarylsiloxanes include polymethylphenyl siloxanes having viscosities of from about 15 to about 65 centistokes at 25° C. These are available, for example, as SF 1075 methyl-phenyl fluid (sold by General Electric Company) and 556 Cosmetic Grade Fluid (sold by Dow Corning Corp.). Useful polyethersiloxane copolymers include, for example, a polyoxyalkylene ether copolymer having a viscosity of about 1200 to 1500 centistokes at 25°C. Such a fluid is available as SF1066 organosilicone surfactant (sold by General Electric Company). Polysiloxane ethylene glycol ether copolymers are preferred copolymers for use in the present compositions.

Non-volatile paraffinic hydrocarbon oils useful in the present invention include mineral oils and certain branched-chain hydrocarbons. Examples of these fluids are disclosed in U.S. Patent 5,019,375 issued to Tanner et al. on May 28, 1991, herein incorporated by reference in its entirety. Preferred mineral oils have the following properties:

- (1) viscosity from about 5 centistokes to about 70 centistokes at 40°C.;
- (2) density between about 0.82 and 0.89 g/cm3 at 25°C.;
- (3) flash point between about 138°C. and about 216°C; and
- (4) carbon chain length between about 14 and about 40 carbon atoms. Preferred branched chain hydrocarbon oils have the following properties:

(1) density between about 0.79 and about 0.89 g/cm3 at 20°C.

- (2) boiling point greater than about 250° C; and
- (3) flash point between about 110°C and about 200°C.

Particularly preferred branched-chain hydrocarbons include Permethyl 103 A, which contains an average of about 24 carbon atoms; Permethyl 104A, which contains an average of about 68 carbon atoms; Permethyl 102A, which contains an average of about 20 carbon atoms; all of which may be purchased from Permethyl Corporation; and Ethylflo 364 which contains a mixture of 30 carbon atoms and 40 carbon atoms and may be purchased from Ethyl Corp.

Additional solvents useful herein are described in US Patent 5,750,096 to Gerald J. Guskey et al., issued May 12, 1998, herein incorporated by reference in its entirety.

Water

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The cosmetic compositions of the present invention preferably comprise water at from about 1% to about 95%, preferably from about 5% to about 90%, most preferably from about 10% to about 85%.

OPTIONAL INGREDIENTS

Shine Control Agents

Cosmetic products that improve and/or regulate the condition of the shiny appearance of skin are increasingly popular with consumers and are referred to herein as "shine control agents". Shine control agents may be included in the compositions of the present invention.

A frequent, undesirable condition is "oily skin", which results from the excessive amount of sebum and sweat that is excreted onto the skin. Sebum is an oily mixture, composed principally of squalene, triglycerides, fatty acids and wax esters. Sebum is produced in the sebaceous glands of the skin. Oily skin is associated with a shiny, undesirable appearance and disagreeable tactile sensation. Sweat is predominantly water with trace quantities of dissolved inorganic salts such as sodium chloride and potassium chloride.

Typically, shine control agents are porous in nature. These agents, when applied to the skin provide a reservoir to absorb excess moisture into the pores, hence reducing the visible quantity of moisture on the skin.

Without being limited by theory, it is believed that it is preferable to combine the use of effective porous, absorbent materials with non-absorbing spherical materials. The latter emphasizes the effect of diffuse reflection over problematic specular reflection, causing an optical modification to the skin and hence a reduction in the shiny appearance of the skin. The combination of absorber and non-absorbing spherical particles is preferable because it allows

development of a product with optimum shine control as well as providing a product with the best tactile sensory performance.

Suitable shine control agents include, but are not limited to, silicas, magnesium aluminum silicates, talc, sericite and various organic copolymers. Particularly effective shine control agents include silicates or carbonates that are formed by reaction of a carbonate or silicate with the alkali (IA) metals, alkaline earth (IIA) metals, or transition metals, and silicas (silicon dioxide). Preferred shine control agents are selected from the group consisting of calcium silicates, amorphous silicas, calcium carbonates, magnesium carbonates, zinc carbonates, and combinations thereof. Some specific examples of the silicates and carbonates useful in this present invention are more fully explained in Van Nostrand Reinhold's Encyclopedia of Chemistry, 4th Ed. pp155, 169, 556, and 849 (1984).

Synthetic versions of the shine control agents, particularly silicates, are preferred. Examples of synthetic silicates useful in the present invention are Hubersorb 250® or Hubersorb 600®, available from JM Huber.

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Shine control agents that primarily comprise silicas are preferred over those materials comprising mainly silicates and/ or carbonates when used for moisture and shine control. Most preferred silicas are in the form of microspheres and/ or ellipsoids, as they have been found to contribute good skin feel characteristics in addition to efficient moisture absorption. Silica ellipsoids useful in the present invention are available from DuPont as ZELEC Sil and Kobo as Silica Shells. Silica microspheres are available from Kobo as MSS-500, MSS500/3, MSS-500H, MSS500/3N, MSS-500N and MSS 500/ 3N; Presperse as Spheron L1500, Spheron P1500. Furned versions of silica can also be used with Aerosil from Degussa and Cab-O-Sil from Cabot both being particularly useful.

Amongst the silicate series, magnesium aluminum silicates are useful, in particular Sebumase, available from Miyoshi Kasei.

When silicas, particularly silica ellipsoids and silica microspheres are intended to be the main means for moisture absorption, it is preferred that the absorbent powder comprise from about 1% to about 40%; more preferably from about 1% to about 25%, and most preferably from about 2% to about 10%, by weight of the composition, of silicas.

Starch-based materials may also be used as shine control agents. Useful examples are Natrosorb W and Natrosorb HFW, DryFlo plus and DryFlo AF pure from National Starch and Chemical Company.

Also found to be useful are methacrylate-based polymeric materials. They can be used

either in conjunction with a dimethicone copolymer or as methacrylate-based copolymers. Specifically, useful examples are: Microsponge 5640 w. Glycerin, Polytrap 6603 available from Enhanced Derm technologies; DSPCS-I2 series and SPCAT-I2 from Kobo; Poly-Pore 200 series from Amcol.

Optionally, yet preferably, the compositions of the present invention contain spherical particles having an average particle size diameter of 10 or greater, preferably greater than 15, more preferably greater than 20 microns. The particle diameter is understood to be that of elementary or primary particles.

Preferred spherical particles include, but are not limited, to polymeric particles chosen from the methylsilsesquioxane resin microspheres such as for example those sold by Toshiba silicone under the name Tospearl 145A; microspheres of polymethylmethacrylates such as those sold by Seppic under the name Micropearl M 100; the spherical particles of crosslinked polydimethylsiloxanes, especially such as those sold by Dow Corning Toray Silicone under the name Trefil E 506C or Trefil E 505C, sphericle particles of polyamide and more specifically Nylon 12, especially such as those sold by Atochem under the name Orgasol 2002D Nat C05, polystyerene microspheres such as for example those sold by Dyno Particles under the name Dynospheres, ethylene acrylate copolymer sold by Kobo under the name FloBead EA209 and mixtures thereof. Also found to be useful is Ronasphere LDP from Kobo Inc

Preferably the spherical particles are present at a concentration of from about 0% to about 40%, more preferably from about 5% to about 35%, most preferably from about 8% to about 30%.

Film Forming Agents

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Film forming agents may be optionally included in the compositions of the present invention to aid film substantivity and adhesion to the skin. Improving the long wear and non-transfer performance of the present compositions is quite desirable. Water-soluble, water insoluble, and water dispersible film forming agents can be used in the internal and external phases of the present compositions to give the desired end benefit.

Preferably, the compositions comprise from about 0% to about 20%, more preferably, from about 0.1% to about 10%, and most preferably, from about 0.1% to about 5%, by weight of the composition, of the film-forming agent.

Suitable film forming agents include:

1) organic silicone resins, fluorinated silicone resins, copolymers of organic

silicone resins, e.g., trimethylsiloxysilicate from GE (SR1000), GE's copolymers of silicone resins, e.g., SF1318 (silicone resin and an organic ester of isostearic acid copolymer) and CF1301 (silicone resin and alpha methyl styrene copolymer), Dow Corning's pressure sensitive adhesives - copolymers of silicone resins and various PDMS's (BIO-PSA series); and 5 acrylic and methacrylic polymers and resins, silicone-acrylate type 2) copolymers and fluorinated versions of, including - silicones plus polymer SA70 from 3M, KP545 from Shin-Etsu, alkyl-acrylate copolymers, e.g., KP 561 and 562 from Shin-Etsu; decene/butene copolymer from Collaborative Labs; 3) 10 polyvinyl based materials, e.g., PVP, PVP/VA, including Antaron/Ganex from 4) ISP (PVP/Triacontene copolymer), Luviskol materials from BASF; polyurethanes, e.g., the Polyderm series from Alzo including but not limited 5) to Polyderm PE/PA, Polyderm PPI-SI-WS, Polyderm PPI-GH, Luviset P.U.R. from BASF; 15 polyquaternium materials, e.g., Luviquat series from BASF 6) acrylates copolymers and acrylates/acrylamide copolymers, e.g., Luvimer and 7) Ultrahold series, both available from BASF; 8) styrene based materials; and chitosan and chitosan based materials including cellulose and cellulose-based 9) 20 materials.

Such film formers are disclosed for example in the International Cosmetic Ingredient Dictionary and Handbook, Seventh Edition, Vol 2, 1636-1638.

25 Skin Conditioning Agent

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Optionally, the compositions of the present invention can further comprise a skinconditioning agent. These agents may be selected from humectants, exfoliants or emollients.

Humectants are polyhydric alcohols intended for moisturizing, reducing scaling and stimulating removal of built-up scale from the skin. Typical polyhydric alcohols include polyalkylene glycols and more preferably alkylene polyols and their derivatives. Illustrative are propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,3-butylene glycol, 1,2,6-hexanetriol, ethoxylated glycerin, propoxylated glycerin and mixtures thereof. Most preferably the humectant is glycerin.

When present, amounts of humectant may range anywhere from 1 to 50%, preferably from 10 to 40%, optimally from 25 to 35% by weight.

Exfoliants according to the present invention may be selected from C2-C30 alpha-hydroxycarboxylic acids, beta-hydroxycarboxylic acids and salts of these acids. Most preferred are glycolic, lactic and salicylic acids and their ammonium salts. Amounts of the exfoliants may range from 1 to 15%, preferably from 2 to 10% by weight.

A wide variety of C2-C30 alpha-hydroxycarboxylic acids may be employed. Suitable examples of which include:

alpha -hydroxyethanoic acid alpha -hydroxypropanoic acid 10 alpha -hydroxyhexanoic acid alpha -hydroxyoctanoic acid alpha -hydroxydecanoic acid alpha -hydroxydodecanoic acid alpha -hydroxytetradecanoic acid 15 alpha -hydroxyhexadecanoic acid alpha -hydroxyoctadecanoic acid alpha -hydroxyeicosanoic acid alpha -hydroxydocosanoic acid alpha -hydroxyhexacosanoic acid, and 20 alpha -hydroxyoctacosanoic acid

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When the conditioning agent is an emollient it may be selected from hydrocarbons, fatty acids, fatty alcohols and esters. Isononyl isononanoate is the most preferred hydrocarbon type of emollient conditioning agent. Other hydrocarbons that may be employed include mineral oil, polyolefins such as polydecene, and paraffins such as isohexadecane (e.g. Permethyl 99 Registered TM and Permethyl 101 Registered TM). Preferably, the compositions of the present invention are substantially free of semi-solid hydrocarbons such as petrolatum, lanolin and lanolin derivatives, sterols (e.g., ethoxylated soya sterols), high molecular weight polybutenes and cocoa butter. By "substantially free," as used herein, means that the concentration of the semi-solid hydrocarbons are preferably less than 10%, more preferably less than 5% most preferably less than 2% and even more preferably 0. Without being limited by theory, such semi-solid hydrocarbons tend to mask the sensory benefits of the siloxane elastomer compositions such as the non-greasy, light feel of the present invention.

Fatty acids and alcohols will have from 10 to 30 carbon atoms. Illustrative of this category are pelargonic, lauric, myristic, palmitic, stearic, isostearic, hydroxystearic, oleic, linoleic, ricinoleic, arachidic, behenic and erucic acids and alcohols.

Oily ester emollients may be those selected from one or more of the following classes:

- 1, Triglyceride esters such as vegetable and animal fats and oils. Examples include castor oil, safflower oil, cottonseed oil, corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, squalene, Kikui oil and soybean oil.
 - 2. Acetoglyceride esters, such as acetylated monoglycerides.

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- 3. Ethoxylated glycerides, such as ethoxylated glyceryl monostearate.
- 4. Alkyl esters of fatty acids having 10 to 20 carbon atoms. Methyl, isopropyl, and butyl esters of fatty acids are useful herein. Examples include hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, diisopropyl adipate, diisohexyl adipate, dihexyldecyl adipate, diisopropyl sebacate, lauryl lactate, myristyl lactate, and cetyl lactate.
- 5. Alkenyl esters of fatty acids having 10 to 20 carbon atoms. Examples thereof include oleyl myristate, oleyl stearate, and oleyl oleate.
 - 6. Ether-esters such as fatty acid esters of ethoxylated fatty alcohols.
- 7. Polyhydric alcohol esters. Ethylene glycol mono and di-fatty acid esters, diethylene glycol mono-and di-fatty acid esters, polyethylene glycol (200-6000) mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol 2000 monooleate, polypropylene glycol 2000 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol polyfatty esters, ethoxylated glyceryl monostearate, 1,2-butylene glycol monostearate, 1,2-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters are satisfactory polyhydric alcohol esters.
 - 8. Wax esters such as beeswax, spermaceti, myristyl myristate, stearyl stearate.
- 9. C1-C30 mono- and poly- esters of sugars and related materials. These esters are derived from a sugar or polyol moiety and one or more carboxylic acid moieties. Depending on the constituent acid and sugar, these esters can be in either liquid or solid form at room temperature. Examples of liquid esters include: glucose tetraoleate, the glucose tetraesters of soybean oil fatty acids (unsaturated), the mannose tetraesters of mixed soybean oil fatty acids, the galactose tetraesters of oleic acid, the arabinose tetraesters of linoleic acid, xylose tetralinoleate, galactose pentaoleate, sorbitol tetraoleate, the sorbitol hexaesters of unsaturated

soybean oil fatty acids, xylitol pentaoleate, sucrose tetraoleate, sucrose pentaoletate, sucrose hexaoleate, sucrose hepatoleate, sucrose octaoleate, and mixtures thereof. Examples of solid esters include: sorbitol hexaester in which the carboxylic acid ester moieties are palmitoleate and arachidate in a 1:2 molar ratio; the octaester of raffinose in which the carboxylic acid ester moieties are linoleate and behenate in a 1:3 molar ratio; the heptaester of maltose wherein the esterifying carboxylic acid moieties are sunflower seed oil fatty acids and lignocerate in a 3:4 molar ratio; the octaester of sucrose wherein the esterifying carboxylic acid moieties are oleate and behenate in a 1:3 molar ratio; and the octaester of sucrose wherein the esterifying carboxylic acid moieties are laurate, linoleate and behenate in a 1:3:4 molar ratio. A preferred solid material is sucrose polyester in which the degree of esterification is 7-8, and in which the fatty acid moieties are C18 mono- and/or di-unsaturated and behenic, in a molar ratio of unsaturates:behenic of 1:7 to 3:5. A particularly preferred solid sugar polyester is the octaester of sucrose in which there are about 7 behenic fatty acid moieties and about 1 oleic acid moiety in the molecule. Other materials include cottonseed oil or soybean oil fatty acid esters of sucrose. The ester materials are further described in, U.S. Patent 2,831,854, U.S. Patent 4,005,196, to Jandacek, issued Jan. 25, 1977; U.S. Patent 4,005,195, to Jandacek, issued Jan. 25, 1977, U.S. Patent 5,306,516, to Letton et al., issued Apr. 26, 1994; U.S. Patent 5,306,515, to Letton et al., issued Apr. 26, 1994; U.S. Patent 5,305,514, to Letton et al., issued Apr. 26, 1994; U.S. Patent 4,797,300, to Jandacek et al., issued Jan. 10, 1989; U.S. Patent 3,963,699, to Rizzi et al, issued Jun. 15, 1976; U.S. Patent 4,518,772, to Volpenhein, issued May 21, 1985; and U.S. Patent 4,517,360, to Volpenhein, issued May 21, 1985.

Amounts of the skin-conditioning agent may range from about 0% to 30%, preferably from about 1% to about 20%, optimally from about 1% to 10% by weight.

Solidifying Agent

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The cosmetic compositions of this invention can contain one or more materials, herein singly or collectively referred to as a "solidifying agent", that are effective to solidify the particular liquid base materials to be used in a cosmetic composition. (As used herein, the term "solidify" refers to the physical and/or chemical alteration of the liquid base material so as to form a solid or semi-solid at ambient conditions, i.e., to form a final composition that has a stable physical structure and is deposited on the skin during normal use conditions.) As is appreciated by those skilled in the art, the selection of the particular solidifying agent for use in the cosmetic compositions will depend upon the particular type of composition desired, i.e., gel or wax-based, the desired rheology, the liquid base material used and the other materials to be used in the

composition. The solidifying agent is preferably present at a concentration of from about 0 to about 90%, more preferably from about 1 to about 50%, even more preferably from about 5% to about 40%, most preferably from about 1% to about 15%.

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Suitable solidifying agents include waxy materials such as candelilla, carnauba waxes, beeswax, spermaceti, carnauba, baysberry, montan, ozokerite, ceresin, paraffin, synthetic waxes such as Fisher-Tropsch waxes, silicone waxes (e.g., DC 2503 from Dow Corning), microcrystalline waxes and the like; soaps, such as the sodium and potassium salts of higher fatty acids, i.e., acids having from 12 to 22 carbon atoms; amides of higher fatty acids; higher fatty acid amides of alkylolamines; dibenzaldehyde-monosorbitol acetals; alkali metal and alkaline earth metal salts of the acetates, propionates and lactates; and mixtures thereof. Also useful are polymeric materials such as, locust bean gum, sodium alginate, sodium caseinate, egg albumin, gelatin agar, carrageenin gum sodium alginate, xanthan gum, quince seed extract, tragacanth gum, starch, chemically modified starches and the like, semi-synthetic polymeric materials such as cellulose ethers (e.g. hydroxyethyl cellulose, methyl cellulose, hydroxypropyl cellulose, cellulose), polyvinylpyrrolidone, propylmethyl hydroxy cellulose, carboxymethyl polyvinylalcohol, guar gum, hydroxypropyl guar gum, soluble starch, cationic celluloses, cationic guars and the like and synthetic polymeric materials such as carboxyvinyl polymers, polyvinylpyrrolidone, polyvinyl alcohol polyacrylic acid polymers, polymethacrylic acid polymers, polyvinyl acetate polymers, polyvinyl chloride polymers, polyvinylidene chloride polymers and the like. Inorganic thickeners may also be used such as aluminum silicates, such as, for example, bentonites, or a mixture of polyethylene glycol and polyethylene glycol stearate or distearate. Naturally occurring polymers or biopolymers and their use are further described in European Application No. 522624, to Dunphy et al. Additional examples of naturally occurring polymers or biopolymers can be found in the Cosmetic Bench Reference, pp. 1.40-1.42, herein incorporated by reference.

Also useful herein are hydrophilic gelling agents such as the acrylic acid/ethyl acrylate copolymers and the carboxyvinyl polymers sold by the B.F. Goodrich Company under the trademark of Carbopol Registered TM resins. These resins consist essentially of a colloidally water-soluble polyalkenyl polyether crosslinked polymer of acrylic acid crosslinked with from 0.75% to 2.00% of a crosslinking agent such as polyallyl sucrose or polyallyl pentaerythritol. Examples include Carbopol 934, Carbopol 940, Carbopol 950, Carbopol 980, Carbopol 951 and Carbopol 981. Carbopol 934 is a water-soluble polymer of acrylic acid crosslinked with about 1% of a polyallyl ether of sucrose having an average of about 5.8 allyl groups for each sucrose

molecule. Also suitable for use herein are carbomers sold under the Trade Name "Carbopol Ultrez 10, Carbopol ETD2020, Carbopol 1382, Carbopol 1342 and Pemulen TR-1 (CTFA Designation: Acrylates/10-30 Alkyl Acrylate Crosspolymer). Combinations of the above polymers are also useful herein. Other gelling agents suitable for use herein include oleogels such as trihydroxystearin.

Hydrophobically modified celluloses are also suitable for use herein. These celluloses are described in detail in U.S. Patents 4,228,277 and 5,104,646, both of which are herein incorporated by reference in their entirety.

Additional examples of suitable gelling agents or gellants can be found in the Cosmetic Bench Reference, p. 1.27, herein incorporated by reference.

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Further examples of suitable solidifying agents disclosed in the following references, all of which are incorporated by reference herein: U.S. Patent 4,151,272, Geary, et al., issued Apr. 24, 1979; U.S. Patent 4,229,432, Geria, issued Oct. 21, 1980; and U.S. Patent 4,280,994, Turney, issued July 28, 1981; "The Chemistry and Technology of Waxes", A. H. Warth, 2nd Edition, reprinted in 1960, Reinhold Publishing Corporation, pp 391-393 and 421; "The Petroleum Chemicals Industry", R. F. Goldstein and A. L. Waddeam, 3rd Edition (1967), E & F. N. Span Ltd., pp 33-40; "The Chemistry and Manufacture of Cosmetics", M. G. DeNavarre, 2nd edition (1970), Van Nostrand & Company, pp 354-376; and in "Encyclopedia of Chemical Technology:, Vol. 24, Kirk-Othmer, 3rd Edition (1979) pp 466-481; U.S. Patent 4,126,679, Davy, et al., issued Nov. 21, 1978; European Patent Specification No. 117,070, May, published Aug. 29, 1984; U.S. Patent 2,900,306, Slater, issued Aug. 18, 1959; U.S. Patent 3,255,082, Barton, issued June 7, 1966; U.S. Patent 4,137,306, Rubino, et al., issued Jan. 30, 1979; U.S. Patent 4,154,816, Roehl, et al., issued May 15, 1979; U.S. Patent 4,226,889, Yuhas, issued Oct. 7, 1980; U.S. Patent 4,346,079, Roehl, issued Aug. 24, 1982; U.S. Patent 4,383,988, Teng, et al., issued May 17, 1983; European Patent Specification No. 107,330, Luebbe, et al., published May 2, 1984; European Patent Specification No. 24,365 Sampson, et al., published Mar. 4, 1981; and U.S. patent application Ser. No. 630,790, DiPietro, filed July 13, 1984.

Preferably, the compositions of the present invention have a hardness value as measured using a TA-XT2i Texture Analyzer (described below) of up to about 25 gram-force, more preferably from about 0.5 to about 20 gram-force, most preferably from about 1 to about 15, optimally from about 1 to about 10 gram-force. Without being limited by theory, it is believed that compositions having stick hardness values above 25 gram-force tend to interfere with the formation of the film structure provided by the polysiloxane elastomer, thus, preventing the

smoothness as well as improved uniformity and evenness of particle distribution within the film. This, in turn, negatively affects the sensory benefits of the cross-linked polysiloxane elastomer component.

Colorant

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Certain embodiments of the present invention contain from about 0% to about 30%, preferably from about 1% to about 20%, more preferably from about 2% to about 15% and most preferably from about 5% to about 15%, of a colorant, on an anhydrous pigment weight basis. These are usually aluminum, barium or calcium salts or lakes. Preferably, dyes are present at from about 0% to about 3% and pearls and the like from 0% to about 10%.

Colorants useful herein are all inorganic and organic colors/pigments suitable for use in cosmetic compositions. When used, pigments are typically dispersed in emollients for the good dispersion of the pigments when incorporated into lip compositions of the present invention, thus providing an even distribution of color. Lakes are either a pigment that is extended or reduced with a solid diluent or an organic pigment that is prepared by the precipitation of a water-soluble dye on an adsorptive surface, which usually is aluminum hydrate. There is uncertainty in some instances as to whether the soluble dye precipitates on the surface of the aluminum hydrate to yield a dyed inorganic pigment or whether it merely precipitates in the presence of the substrate. A lake also forms from precipitation of an insoluble salt from an acid or basic dye. Calcium and barium lakes are also used herein.

Lakes suitable for use in the present invention include Red 3 Aluminum Lake, Red 21 Aluminum Lake, Red 27 Aluminum Lake, Red 28 Aluminum Lake, Red 33 Aluminum Lake, Yellow 5 Aluminum Lake, Yellow 6 Aluminum Lake, Yellow 10 Aluminum Lake, Orange 5 Aluminum Lake and Blue 1 Aluminum Lake, Red 6 Barium Lake, Red 7 Calcium Lake.

Other colors can also be included in the lipsticks, such as dyes. Suitable examples include Red 6, Red 21, Brown, Russet and Sienna dyes and mixtures thereof.

There are no specific limitations as to the pigment, colorant or filler powders used in the composition. Each may be a body pigment, inorganic white pigment, inorganic colored pigment, pearling agent, and the like. Specific examples are talc, mica, magnesium carbonate, calcium carbonate, magnesium silicate, aluminum magnesium silicate, silica, titanium dioxide, zinc oxide, red iron oxide, yellow iron oxide, black iron oxide, ultramarine, polyethylene powder, methacrylate powder, polystyrene powder, silk powder, crystalline cellulose, starch, titanated mica, iron oxide titanated mica, bismuth oxychloride, and the like.

Additional pigment/powder fillers include, but are not limited to, inorganic powders such as gums, chalk, Fuller's earth, kaolin, sericite, muscovite, phlogopite, synthetic mica, lepidolite, biotite, lithia mica, vermiculite, aluminum silicate, starch, smectite clays, alkyl and/or trialkyl aryl ammonium smectites, chemically modified magnesium aluminum silicate, organically modified montmorillonite clay, hydrated aluminum silicate, fumed aluminum starch octenyl succinate barium silicate, calcium silicate, magnesium silicate, strontium silicate, metal tungstate, magnesium, silica alumina, zeolite, barium sulfate, calcined calcium sulfate (calcined gypsum), calcium phosphate, fluorine apatite, hydroxyapatite, ceramic powder, metallic soap (zinc stearate, magnesium stearate, zinc myristate, calcium palmitate, and aluminum stearate), colloidal silicone dioxide, and boron nitride; organic powder such as polyamide resin powder (nylon powder), cyclodextrin, methyl polymethacrylate powder, copolymer powder of styrene and acrylic acid, benzoguanamine resin powder, poly(ethylene tetrafluoride) powder, and carboxyvinyl polymer, cellulose powder such as hydroxyethyl cellulose and sodium carboxymethyl cellulose, ethylene glycol monostearate; inorganic white pigments such as magnesium oxide. Other useful powders are disclosed in U.S. Patent 5, 688,831, to El-Nokaly et al., issued November 18, 1997, herein incorporated by reference in its entirety. These pigments and powders can be used independently or in combination.

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Also useful herein are pigment and/or dye encapsulates such nanocolorants from BASF and multi-layer interference pigments such as Sicopearls from BASF.

It is preferred that the pigments/powders are surface treated to provide added stability of color and ease of formulation. Hydrophobically treated pigments are more preferred, because they may be more easily dispersed in the solvent/oil phase. In addition, it may be useful to treat the pigments with a material that is compatible with a silicone phase. Particularly useful hydrophobic pigment treatments for use in water-in-silicone emulsions include polysiloxane treatments such as those disclosed in U.S. Patent 5,143,722, incorporated herein by reference in its entirety. Also preferred are pigment/powders having a primary average particle size of from about 5 nm to about 100,000 nm, more preferably from about 50nm to about 5,000 nm, most preferably from about 100nm to about 1000nm. Mixtures of the same or different pigment/powder having different particle sizes are also useful herein (e.g., incorporating a TiO2 having a primary particle size of from about 10 nm to about 400 nm with a TiO2 having a primary particle size of from about 10 nm to about 50 nm).

Dispersants may also be used in conjunction with the colors and pigments of the present invention. Examples of suitable dispersants include, but are not limited to, those described in U.S. Patent 5,688,493, herein incorporated by reference in its entirety.

Preservatives

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Suitable traditional preservatives for compositions of this invention are alkyl esters of para-hydroxybenzoic acid. Other preservatives that have more recently come into use include hydantoin derivatives such as 1,3-bis(hydroxymethyl)-5,5-dimthylhydantoin, propionate salts, and a variety of quaternary ammonium compounds such as benzalkonium chloride, quaternium 15 (Dowicil 200), benzethonium Chloride, and methylbenzethonium chloride. Cosmetic chemists are familiar with appropriate preservatives and routinely choose them to satisfy the preservative challenge test and to provide product stability. Particularly preferred preservatives are disodium EDTA, phenoxyethanol, methyl paraben, propyl paraben, imidazolidinyl urea (commercially available as Germall 1157), sodium dehydroacetate and benzyl alcohol. The preservatives should be selected having regard for the use of the composition and possible incompatibilities between the preservatives and other ingredients in the emulsion. Preservatives preferably are employed in amounts ranging from about 0% to about 5%, more preferably from about 0.01% to about 2.5%, and most preferably from about 0.01% to about 1%, by weight of the composition.

Emulsifiers

In addition to the emulsifying crosslinked siloxane elastomer, other emulsifiers or surfactants can be used herein. These emulsifiers may be nonionic, anionic or cationic. Suitable emulsifiers are disclosed in, for example, U.S. Patent 3,755,560, issued Aug. 28, 1973, Dickert et al.; U.S. Patent 4,421,769, issued Dec. 20, 1983, Dixon et al.; and McCutcheon's Detergents and Emulsifiers, North American Edition, pages 317-324 (1986), each incorporated herein by reference in its entirety. Illustrative nonionic surfactants are alkoxylated compounds based on C10-C22 fatty alcohols and acids, and sorbitan. These materials are available, for instance, from the Shell Chemical Company under the Neodol trademark, Copolymers of polyoxypropylene-polyoxyethylene, sold by the BASF Corporation under the Pluronic trademark, are sometimes also useful. Alkyl polyglycosides available from the Henkel Corporation may also be utilized for purposes of this invention. Anionic type emulsifiers or surfactants include fatty acid soaps, sodium lauryl sulphate, sodium lauryl ether sulphate, alkyl benzene sulphonate, mono- and dialkyl acid phosphates and sodium fatty acyl isethionate. Amphoteric emulsifiers or surfactants

include such materials as dialkylamine oxide and various types of betaines (such as cocamidopiopyl betaine).

Preferred for use herein are polyoxyalkylene copolymers also known as silicone polyethers. Polymers are described in detail in U. S. Patent 4,268,499, which is incorporated herein by reference in its entirety. A particularly preferred polyoxyalkylene copolymer is known by its CTFA designation as dimethicones copolyol. A particularly preferred form of dimethicone copolyol is that supplied by Dow Corning as DC5225C.

The overall concentration of the emulsifier can be from 0% to about 10% of the formulation, preferably from 0.1% to about 5% and most preferably from about 0.1% to about 2%, by weight of the composition. Examples of suitable emulsifiers can be found in U.S. Patent 5,085,856 to Dunphy et al.; Japanese Patent Publication Sho 61-83110; European Patent Application EP 522624 to Dunphy et al.; U.S. patent 5,688,831 to El-Nokaly et al.; and Examples of suitable moistures can be found in Cosmetic Bench Reference, pp. 1.22, 1.24-1.26 (1996), all of which are herein incorporated by reference in their entirety.

Organic Sunscreens

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Compositions of the present invention preferably comprise an organic sunscreen. Suitable sunscreens can have UVA absorbing properties, UVB absorbing properties or a mixture thereof. The exact amount of the sunscreen active will vary depending upon the desired Sun Protection Factor, i. e., the "SPF" of the composition as well as the desired level of UVA protection. The compositions of the present invention preferably comprise an SPF of at least 10, preferably at least 15. (SPF is a commonly used measure of photoprotection of a sunscreen against erythema. The SPF is defined as a ratio of the ultraviolet energy required to produce minimal erythema on protected skin to that required to products the same minimal erythema on unprotected skin in the same individual. See Federal Register, 43, No 166, pp. 38206-38269, August 25, 1978). Compositions of the present invention preferably comprise from about 2% to about 20%, more typically from about 4% to about 14%, by weight, of organic sunscreen. Suitable sunscreens include, but are not limited to, those found in the CTFA International Cosmetic Ingredient Dictionary and Handbook, 7th edition, volume 2 pp. 1672, edited by Wenninger and McEwen (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D. C., 1997).

The compositions of the present invention preferably comprise a UVA absorbing sunscreen actives that absorb UV radiation having a wavelength of from about 320nm to about 400nm. Suitable UVA absorbing sunscreen actives are selected from dibenzoylmethane

derivatives, anthranilate derivatives such as methylanthranilate and homomethyl, 1-N-acetylanthranilate, and mixtures thereof. Examples of dibenzoylmethane sunscreen actives are described in US Patent No 4,387,089 issued to Depolo; and in Sunscreens: Development, Evaluation, and Regulatory Aspects edited by N. J. Lowe and N. A. Shaath, Marcel Dekker, Inc (1990). The UVA absorbing sunscreen active is preferably present in an amount to provide broad-spectrum UVA protection either independently, or in combination with, other UV protective actives that may be present in the composition.

Preferred UVA sunscreen actives are dibenzoylmethane sunscreen actives and their derivatives. They include, but are not limited to, those selected from 2-methyldibenzoylmethane, 4-methyldibenzoylmethane, 4-isopropyldibenzoylmethane, 4-tert-butyldibenzoylmethane, 2, 4dimethyldibenzoylmethane, 2, 5-dimethyldibenzoylmethane, 4, 4'-diisopropylbenzoylmethane, 4-1-dimethylethyl)-4'-methoxydibenzoylmethane, 2-methyl-5-isopropyl-4'-(1, methoxydibenzoylmethane, 2-methyl-5-tert-butyl-4'-methoxy-dibenzoylmethane, 2, 4-dimethyl-4'-methoxydibenzoylmethane, 2, 6-dimethyl-4'-tert-butyl-4'methoxydibenzoylmethane, and mixtures thereof. Preferred dibenzoyl sunscreen actives include those selected from 4-(1, 1dimethylethyl)-4'-methoxydibenzoylmethane, 4-isopropyldibenzoylmethane, and mixtures 4-(1, 1-dimethylethyl)-4'-A more preferred sunscreen active is thereof. methoxydibenzoylmethane.

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The sunscreen active 4-(1, 1-dimethylethyl)-4'-methoxydibenzoylmethane, which is also known as butyl methoxydibenzoylmethane or Avobenzone, is commercially available under the names of Parsol® 1789 from Givaudan Roure (International) S. A. (Basel, Switzerland) and Eusolex® 9020 from Merck & Co., Inc (Whitehouse Station, NJ). The sunscreen 4-isoproplydibenzoylmethane, which is also known as isopropyldibenzoylmethane, is commercially available from Merck under the name of Eusolex® 8020.

The compositions of the present invention preferably further comprise a UVB sunscreen active that absorbs UV radiation having a wavelength of from about 290nm to abut 320nm. The compositions preferably comprise an amount of the UVB sunscreen active that is safe and effective to provide UVB protection either independently, or in combination with, other UV protective actives that may be present in the compositions. The compositions preferably comprise from about 0.1% to abut 16%, more preferably from about 0.1% to about 12%, and most preferably from about 0.5% to about 8% by weight, of UVB absorbing organic sunscreen.

A wide variety of UVB sunscreen actives are suitable for use herein. Nonlimiting examples of such organic sunscreen actives are described in US Patent No 5,087,372 issued

February 11, 1992 to Haffey et al.; and US Patent Nos 5,073,371 and 5,073,372 both issued on December 17, 1991 to Turner et al.. Preferred UVB sunscreen actives are selected from 2-ethylhexyl-2-cyano-3, 3-diphenylacrylate (referred to as octocrylene), 2-phenyl-benzimidazole-5-sulphonic acid (PBSA), cinnamates and their derivatives such as 2-ethylhexyl-p-methoxycinnamate and octyl-p-methoxycinnamate, TEA salicylate, octyldimethyl PABA, camphor derivatives and their derivatives, and mixtures thereof. Preferred organic sunscreen actives are 2-ethylhexyl-2-cyano-3, 3-diphenylacrylate (referred to as octocrylene), 2-phenyl-benzimidazole-5-sulphonic acid (PBSA), octyl-p-methoxycinnamate, and mixtures thereof. Salt and acid neutralised forms of the acidic sunscreens are also useful herein. When organic sunscreen salts, such as PBSA, are used within compositions of the present invention they can disrupt the action of the thickener with the result that the final product may have sub optimal rheology. This can be countered by the addition of higher levels of thickener, fatty alcohols or nonionic surfactants such that the rheology of the final product returns to the desired level.

An agent may also be added to any of the compositions useful in the present invention to stabilise the UVA sunscreen to prevent it from photo-degrading on exposure to UV radiation and thereby maintaining its UVA protection efficacy. Wide ranges of compounds have been cited as providing these stabilising properties and should be chosen to compliment both the UVA sunscreen and the composition as a whole. Suitable stabilising agents include, but are not limited to, those described in US Patents Nos 5,972,316; 5,968,485; 5,935,556; 5,827,508 and Patent WO 00/06110. Preferred examples of stabilising agents for use in the present invention include 2-ethylhexyl-2-cyano-3, 3-diphenylacrylate (referred to as octocrylene), ethyl-2-cyano-3, 3-diphenylacrylate, ethyl-3, 3-bis(4-methoxyphenyl)acrylate, and mixtures thereof. 2-ethylhexyl-2-cyano-3, 3-diphenylacrylate is most preferred.

An agent may also be added to any of the compositions useful in the present invention to improve the skin substantivity of those compositions, particularly to enhance their resistance to being washed off by water, or rubbed off. A preferred agent that will provide this benefit is a copolymer of ethylene and acrylic acid. Compositions comprising this copolymer are disclosed in U.S. Patent 4,663,157, Brock, issued May 5, 1987.

Inorganic Sunscreens

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In addition to the organic sunscreens compositions of the present invention can additionally comprise inorganic physical sunblocks. Nonlimiting examples of suitable physical sunblocks are described in CTFA International Cosmetic Ingredient Dictionary, 6th Edition, 1995, pp. 1026-28 and 1103, Sayre, R. M. et al., "Physical Sunscreens", J. Soc. Cosmet. Chem., Vol 41,

no 2, pp. 103-109 (1990). Preferred inorganic physical sunblocks are zinc oxide and titanium dioxide, and mixtures thereof.

When used, the physical sunblocks are present in an amount such that the present compositions are transparent on the skin (i.e. non-whitening), preferably less than or equal to about 5%. When titanium dioxide is used, it can have an anatase, rutile, or amorphous structure. Physical sunblock particles, e.g. titanium dioxide and zinc oxide, can be uncoated or coated with a variety of materials including but not limited to amino acids, aluminum compounds such as alumina, aluminum stearate, aluminum laurate, and the like; carboxylic acids and their salts e.g. stearic acid and its salts; phospholipids such as lecithin; organic silicone compounds; inorganic silicone compounds such as silica and silicates; and mixtures thereof. A preferred titanium dioxide is commercially available from Tayca (Japan) and is distributed by Tri-K Industries (Emerson, NJ) under the MT micro-ionized series (e.g. MT 100SAS).

The compositions of the present invention preferably comprise from about 0.1% to about 10%, more preferably from about 0.1% to about 4%, and most preferably from about 0.5% to about 2.5%, by weight, of inorganic sunscreen.

Aerated Compositions

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Optionally and preferably, the compositions of the present invention are aerated. By "aerated" as used herein means the air is incorporated either by hand, mechanical mixing or by using any other form of conventional foaming or whipping instrument technology. Preferably the compositions of the present invention contain at least about 1%, preferably at least about 2%, optimally from about 3 to about 5% air.

Other Optional Ingredients

A variety of additional ingredients can be incorporated into the compositions of the present invention. Nonlimiting examples of these additional ingredients include additional skin care actives such as peptides (e.g., Matrixyl [pentapetide derivative]), farnesol, bisabolol, phytantriol, glycerol, urea, guanidine (e.g., amino guanidine); vitamins and derivatives thereof such ascorbic acid, vitamin A (e.g., retinoid derivatives such as retinyl palmitate or retinyl proprionate), vitamin E (e.g., tocopherol acetate), vitamin B₃ (e.g., niacinamide) and vitamin B₅ (e.g., panthenol) and the like and mixtures thereof; sunscreens; anti-acne medicaments (resorcinol, salicylic acid, and the like; antioxidants (e.g., phytosterols, lipoic acid); flavonoids (e.g., isoflavones, phytoestrogens); skin soothing and healing agents such as aloe vera extract, allantoin and the like; chelators and sequestrants; and agents suitable for aesthetic purposes such as essential oils, fragrances, skin sensates, opacifiers, aromatic compounds (e.g., clove oil,

menthol, camphor, eucalyptus oil, and eugenol). Nonlimiting examples of suitable carboxylic copolymers, emulsifiers, emollients, and other additional ingredients are disclosed in U.S. Patent 5,011,681, to Ciotti et al., issued April 30, 1991 and US Patent 5,939,082, to Oblong et al., issued August 17, 1999, both of which are herein incorporated by reference. The above-mentioned vitamin B₃ compounds can be incorporated as re-crystallized crystals that remain in crystalized form in the composition or as partially solubilize crystals (i.e., some of the crystals are dissolved and some remain in crystalline form in the composition.).

Analytical Test Methods

Determination of Particle Size

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Samples are prepared placing approximately 1 gram of the cross-linked elastomer (gel) in a small bottle with approximately 30 grams of a 1:1 isopropyl alcohol:dimethicone (DC 245) solution (IPA:DC245). The 1:1 IPA:DC245 solution is passed through a 0.2 µm syringe filter to remove foreign particulates (e.g., dust). The sample is then mixed (to disperse elastomer) using a Glass-Col Tissue Culture Rotator set at 70% for approximately 5 days.

The samples were, next, measured using a Horiba LA-910 equipped with a fraction cell holder and a magnetic stir bar. For a blank, a separate sample was prepared containing only the 30 grams 1:1 IPA:DC245. Before measurement, 10ml aliquots of the prepared samples were placed in a small vial and allowed to settle for 30 minutes (to separate out large agglomerates). Stirring was used during measurement and the sampling time was set at 25 sec., the data were reported on a Volume basis using a relative refractive index of 1.06-0.00i. Samples are further diluted with 1:1 IPA:DC245 as necessary to achieve concentrations within the working range for the Horiba LA-910. More detailed instructions can be found in the Operator's Manuel for the Horiba LA 910, herein incorporated by reference. The process is additionally described in US Patent 5,998,542 and US Patent 5,929,162, both of which are herein incorporated by reference in their entirety

Hardness Value Test

The term "product hardness" as used herein is a reflection of how much force is required to move a rod a specified distance and at a controlled rate into a cosmetic composition under the following test conditions. Higher values represent harder product, and lower values represent softer product. These values are measured at 27°C, 15% relative humidity, using a TA-XT2i Texture Analyzer, available from Texture Technology Corp., Scarsdale, New York, U.S.A. The product hardness value as used herein represents the amount of force required to move a 16mm long stainless steel rod having a 0.254mm diameter through the composition for a distance of

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12.2mm at a rate of 0.85mm/second. The rod is attached to the instrument by means of a suitable adapter (e.g., drill-type chuck). Other test parameters include: Pre-Test Speed of 0.85 mm/s, Post Test Speed of 1.70 mm/s, trigger distance of 0.1mm. More detailed instructions can be found in the Operator's Manuel for the TA-XT2i, herein incorporated by reference.

ASSOCIATED METHODS

Applicants have found that the compositions of the present invention are useful in a variety of applications directed to enhancement of mammalian skin. The methods of use for the compositions disclosed and claimed herein include, but are not limited to: 1) methods of increasing the substantivity of a cosmetic to skin; 2) methods of moisturizing skin; 3) methods of improving the natural appearance of skin; 4) methods of applying a color cosmetic to skin; 5) methods of preventing, retarding, and/or treating wrinkles; 6) methods of providing UV protection to skin; 7) methods of preventing, retarding, and/or controlling the appearance of oil; 8) methods of modifying the feel and texture of skin; 9) methods of providing even skin tone; 10) methods of preventing, retarding, and/or treating the appear of spider vessels and varicose veins; 11) methods of masking the appearance of vellus hair on skin; and 12) methods of concealing blemishes and/or imperfections in human skin, including acne, age spots, freckles, moles, scars, under eye circles, birth marks, post-inflammatory hyperpigmentation, etc.. Each of the methods discussed herein involve topical application of the claimed compositions to skin.

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLES

The cosmetic products in the following examples illustrate specific embodiments of the cosmetic compositions of the present invention, but are not intended to be limiting thereof. The skilled artisan can undertake other modifications without departing from the spirit and scope of this invention. All exemplified compositions can be prepared by conventional formulation and mixing techniques. Component amounts are listed as weight percents and may exclude minor materials such as diluents, filler, and so forth. The listed formulations, therefore, comprise the listed components and any minor materials associated with such components.

Example I

A lipstick composition of the present invention is prepared as follows:

Ingredient Wt%

Саглаива	1.50
Ozokerite	5.50
Candelilla	4.00
Hydrogenated Vegetable Oil	8.50
Acetylated Lanolin	4.00
Propylparaben	0.10
Cetyl Ricinoleate	10.00
Ascorbyl Palmitate	1.00
Polybutene	2.00
Polysiloxane Copolymer ¹	5.97
Stearyl Dimethicone (DC 2503 Cosmetic	5.97
wax)	
Anhydrous Lanolin	5.97
KSG 21 ² Elastomer gel	2.95
GE SFE 839 Elastomer gel ³	20.00
Association Structure Phase	·
Lecithin	5.00
Niacinamide	2.50
Panthenol	1.00
Glycerine	4.04
Pigment	9.00
Water	6.00

¹ #1154-141-1, supplied by GE Silicones.

The ingredients for the Association Structure Phase, except for the pigments, are mixed until association structures are formed. Once the association structures are formed, the pigments are added and milled on a three-roll mill. The mixture is then mixed with the remaining ingredients and mixed until a homogeneous mixture is achieved. (Or, alternatively, the above

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² 25% Dimethicone/copolyol Crosspolymer in dimethicone.

³ 5% Dimethicone/Vinyl Dimethicone crosspolymer (aver. particle size of at least 20 microns) in cyclomethicone

components are added and mixed together at the same time.) This mixture is heated to 85°C and then poured into a mold at room temperature.

The lipstick is applied to the lips to provide color, moisturization and improved lip feel.

Example II

A mascara of the present invention is prepared as follows:

Ingredient	<u>Wt.%</u>
Carnauba Wax	3.00
Glyceryl Monostearate ¹	7.50
White Beeswax	3.75
C18-C36 Triglycerides ²	5.50
Hydrogenated Glycerol Rosinate ³	0.15
Propylparaben	0.10
Paraffin Wax 118/125	2.25
Paraffin Wax	2.25
Elastomer Gel (KSG21) ⁴	2.31
DC9040 Elastomer gel ⁷	15.00
Lecithin ⁵	2.25
Stearic Acid 3X	4.00
Oleic Acid	0.75
Triethanolamine	1.25
Potassium Cetyl Phosphate ⁶	1.00
Shellac, NF	3.00
Triethanolamine	0.47
Trisodium EDTA	0.10
Black Iron Oxide	7.00
Simethicone	0.20
Methylparaben	0.20
Ethylparaben	0.15
Phenoxyethanol	0.80
Ethyl Alcohol 40B, 190 proof	4.00
Diazolidinyl Urea	0.20

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Deionized Water	30.22
dl-Panthenol	0.35
niacinamide	2.25
Total	100.00

¹ Available as Emerest 2400 available form Henkel/Emery -

The waxes and fats are mixed in a vessel equipped with a heating source. The waxes and fats are heated and mixed at low speed using a conventional blender to liquify the mixture. The mixing is continued until the mixture is homogeneous. To the homogeneous mixture is added the pigments. The mixing rate is increased to high and the pigments are mixed into the mixture for about 30-35 minutes until uniformly dispersed. The mixing is continued while adding emulsifiers.

In a second vessel equipped with a heating source is added water followed by the niacinamide, lecithin and any other water-dispersible components. The mixture is heated and mixed to a temperature of from about 80-95°C. Additional water is added as necessary to account for water loss.

The aqueous and lipophilic mixtures are combined and mixed using a dispersator type mixer. Mixing is continued until the mixture cools to a temperature of from about 65-70°C. Elastomer gels and preservatives are added with mixing, allowing the mixture to cool further to 45-47°C. Any remaining components are added with mixing. The combined mixture is cooled to a temperature above the solidification point and is then poured into suitable containers.

The mascara composition is applied to the lashes and/or eyebrows to provide softening, moisturization and conditioning.

Example III

A moisturizing lotion of the present invention is prepared as follows:

² Available as Syncrowax HGL-C available from Croda, Inc. -

³ Available as Foral 105 available from Hercules, Inc. -

⁴25% Dimethicone/Copolyol Crosspolymer in dimethicone

⁵ Available as Centrolex F available from Central Soya, Inc. -

⁶ Available as Amphisol K available from Givaudan -

⁷ 12% Dimethicone/Vinyl Dimethicone crosspolymer(aver. particle size of at least 20 microns) in cyclomethicone

Ingredient	Wt %
Cyclomethicone (DC245)	17.35
DC9040 Elastomer gel ²	18.00
Elastomer Gel (KSG21) ¹	18.33
Propylparaben	0.20
Ethylene/Acrylic Acid Copolymer	10.00
microspheres (Flobeads EA 209	
supplied by Kobo Products Inc.)	
Glycerin	25.00
Water	8.00
Niacinamide	3.00
Methylparaben	0.12
Total	100.00

¹25% Dimethicone/Copolyol Crosspolymer in dimethicone

In a suitable stainless steel vessel, the cyclomethicone, DC9040, KSG21 and propylparaben are added with mixing using conventional mixing technology and mixed until homogeneous. In a separate vessel, the niacinamide and water are mixed using conventional mixing technology until homogeneous. To the niacinamide solution is next added the glycerin, ethylene/acrylic acid copolymer microspheres and methylparaben with mixing until homogeneous. Next, the niacinamide mixture is combined with the cyclomethicone mixture and mixed using conventional mixing technology until homogeneous. The combined mixture is then poured into suitable containers.

The moisturizing cosmetic lotion is applied to the face and/or body to provide softening, moisturization and conditioning.

Example IV

A liquid foundation of the present invention is prepared as follows:

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² 12% Dimethicone/Vinyl Dimethicone crosspolymer (aver. particle size of at least 20 microns) in cyclomethicone

Ingredient	Wt%
Cyclomethicone	11.62
Dimethicone copolyol emulsifier	0.70
KSG32 Elastomer Gel ¹	5.38
GE SFE839 Elastomer gel ²	10.00
Isononyl Isononanoate	5.00
n-Propyl-4-hydroxybenzoic Acid	0.20
Ethylene Brassylate	0.03
Titanium Dioxide	17.8
Yellow Iron Oxide	1.70
Red Iron Oxide	0.19
Black Iron Oxide	0.11
Methylparahydroxybenzoate	0.12
Glycerin	10.00
2-amino-2-methyl-1-propanol	0.10
Water	36.45
sucrose oleate ester	0.60
Total	100.00

¹25%% Lauryl Dimethicone/Copolyol Crosspolymer in isododecane

In a suitable stainless steel vessel, the cyclomethicone, dimethicone copolyol, GE SFE 839, KSG32, isononyl isononanoate, n-propyl-4-hydroxybenzoic acid, and ethylene brassylate are added with mixing using conventional mixing technology and mixed until homogeneous. In a separate vessel equipped with a heat source, the sucrose oleate ester and water are heated to 50°C and mixed using conventional mixing technology until homogeneous. The sucrose oleate ester mixture is then allowed to cool to room temperature. Once cooled, the titanium dioxide, iron oxides, methylparahydroxy benzoate, glycerin and 2-amino-2-methyl-1-propanol are added to sucrose oleate ester mixture with mixing to form a homogeneous, pigment slurry. Next, the sucrose oleate ester mixture is combined with the cyclomethicone mixture and mixed using

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² 5% Dimethicone/Vinyl Dimethicone crosspolymer (aver. particle size of at least 20 microns) in cyclomethicone

conventional mixing technology until homogeneous. The combined mixture is then poured into suitable containers.

The liquid foundation is applied to the face to provide softening, moisturization and conditioning.

Example V

A line-minimizing product that improves the appearance of skin texture is prepared as follows:

<u>Ingredient</u>	<u>Wt%</u>
DC9040 cross linked	50.25
elastomer gel ¹	
Elastomer gel (KSG 21) ²	5.00
Cyclomethicone (DC245)	10.00
Silica, titanium dioxide, iron	8.00
oxide	
(Ronasphere LDP)	
Isoeicosane (Permethyl	5.00
102A)	
Alkyl methicone (DC AMS	1.50
C30 wax)	
Propylparabens	0.25
Tocopherol acetate	0.50
Water	9.35
Glycerin	7.00
Niacinamide	2.00
Panthenol	0.50
Sodium dehydroacetate	0.30
Disodium EDTA	0.10
Phenoxyethanol	0.25

¹ 12% Dimethicone/Vinyl Dimethicone crosspolymer (aver. particle size of at least 20 microns) in cyclomethicone

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 $^{^2}$ 25% Dimethicone/Copolyol Crosspolymer in dimethicone $\,$

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In a suitable vessel, add the water, glycerine, niacinamide, panthenol, sodium dehydroacetate, disodium EDTA and phenoxyethanol. They are mixed using conventional technology until a clear water phase is achieved.

In a separate vessel equipped with a heating source, the AMS wax and Permethyl are added and heated to 75 deg C with gentle mixing. In a third vessel, the Ronasphere, and cyclomethicone (DC245) are added with gentle mixing to form the Ronasphere/DC245 pre-mix. Once the wax/Permethyl mixture is fully molten, the DC9040 and KSG21 elastomers are added and this mixture and mixed until homogeneous. The wax/Permethyl/elastomer mixture is mixed using a Heidolph overhead stirrer (Model #RZR50), or equivalent, on low speed (about 50-100 rpms) while cooling the mixture to room temperature. Once the wax/Permethyl mixture is cooled to room temperature, the Ronasphere/DC245 pre-mix and the propylparabens and tocopherol acetate are added and the combined mixture is milled using a Turrax T25 on low speed (about 8000 rpms) until homogeneous to form the lightly colored phase.

Next, the clear water phase and the colored phase are combined and milled using a Turrax T25 on low speed (about 8000 rpms) until the water is full incorporated and an emulsion is formed. The resultant composition is then incorporated into the appropriate package.

 $\underline{\text{Example VI}}$ A liquid foundation of the present invention is prepared as follows:

Ingredient	<u>Wt%</u>
DC9040 cross linked	46.25
elastomer gel	
Elastomer gel (KSG 21) ²	5.00
Cyclomethicone (DC245)	10.00
Iron oxides - silicone	4.00
coated	
Titanium dioxide - silicone	8.00
coated	
Propylparabens	0.25
Tocopherol acetate	0.50
Isoeicosane (Permethyl	5.00
102A)	

Alkyl methicone (DC	1.50
AMS C30 wax)	
Water	9.35
Glycerin	7.00
Niacinamide	2.00
Panthenol	0.50
Sodium dehydroacetate	0.30
Disodium EDTA	0.10
Phenoxyethanol	0.25

¹ 12% Dimethicone/Vinyl Dimethicone crosspolymer (aver. particle size of at least 20 microns) in cyclomethicone

In a suitable vessel, the water, glycerine, niacinamide, panthenol, sodium dehydroacetate, disodium EDTA and phenoxyethanol are added and mixed using conventional technology until a clear water phase is achieved.

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In a separate vessel, he AMS wax and the Permethyl are added and heated to 75 deg C with gentle mixing. In a third vessel, the iron oxide, titanium dioxides and cyclomethicone (DC245) are added and milled using high shear (about 20,000 units) to deagglomerate the pigments, forming an iron oxides/titanium dioxide/DC245 pre-mix. Once the wax/Permethyl mixture is fully molten, the DC9040 and KSG21 elastomers are added to this mixture and mixed until homogeneous. The wax/Permethyl/elastomer mixture is mixed using a Heidolph overhead stirrer (model #RZR50), or equivalent, on low speed (about 50-100rpms) while cooling the mixture to room temperature. Once wax/Permethyl/elastomer mixture is cooled to room temperature, the propylparabens and tocopherol acetate and the iron oxides/titanium dioxide/DC245 pre-mix are added and combined mixture is milled using a Turrax T25 on low speed (about 8000 rpms) until homogeneous to form the colored phase.

Next, the clear water phase and the colored phase are combined and milled using a Turrax T25 on low speed (about 8000 rpms) until the water is full incorporated and an emulsion is formed. Then incorporate into the appropriate package.

Example VII

A line-minimizing product that improves the appearance of skin texture is prepared as follows:

² 25% Dimethicone/Copolyol Crosspolymer in dimethicone

Ingredient	Wt%
DC9040 cross linked	50.25
elastomer gel ¹	
Elastomer gel (KSG 21) ²	5.00
Cyclomethicone (DC245)	10.00
Ethylene acrylates	8.00
copolymer	
(EA209)	
Isoeicosane (Permethyl	5.00
102A)	
Alkyl methicone (DC AMS	1.50
C30 wax)	
Propylparabens	0.25
Tocopherol acetate	0.50
Water	9.35
Glycerin	7.00
Niacinamide	. 2.00
Panthenol	0.50
Sodium dehydroacetate	0.30
Disodium EDTA	0.10
Phenoxyethanol	0.25

¹ 12% Dimethicone/Vinyl Dimethicone crosspolymer (aver. particle size of at least 20 microns) in cyclomethicone

In a suitable vessel, add the water, glycerine, niacinamide, panthenol, sodium dehydroacetate, disodium EDTA and phenoxyethanol. They are mixed using conventional technology until a clear water phase is achieved.

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In a separate vessel equipped with a heating source, the AMS wax and Permethyl are added and heated to 75 deg C with gentle mixing. In a third vessel, the EA209, and cyclomethicone (DC245) are added with gentle mixing to form the EA209/DC245 pre-mix. Once the wax/ Permethyl mixture is fully molten, the DC9040 and KSG21 elastomers are added and

² 25% Dimethicone/Copolyol Crosspolymer in dimethicone

this mixture and mixed until homogeneous. The wax/Permethyl/elastomer mixture is mixed using a Heidolph overhead stirrer (Model # RZR50), or equivalent, on low speed (about 50-100rpms) while cooling the mixture to room temperature. Once the wax/Permethyl/elastomer mixture is cooled to room temperature, the EA209/DC245 pre-mix and the propylparabens and tocopherol acetate are added and the combined mixture is milled using a Turrax T25 on low speed (about 8000 rpms) until homogeneous to form the colored phase.

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Next, the clear water phase and the colored phase are combined and milled using a Turrax T25 on low speed (about 8000 rpms) until the water is full incorporated and an emulsion is formed. The resultant composition is then incorporated into the appropriate package.

Example VIII

A liquid make-up with SPF is made by mixing the following ingredients as detailed below.

	
Ingredient	<u>Wt%</u>
Non-emulsifying elastomer gel (DC9040)	40.00
Emulsifying elastomer gel (KSG 21)	5.00
Cyclomethicone (DC245)	13.63
Isoeicosane (Permethyl 102A)	5.00
Titanium dioxide	8.00
Iron oxides	2.50
Butylmethoxydibenzoylmethane	1.00
Octylsalicylate	2.00
Octocrylene	0.50
Propylparabens	0.10
Ethylparabens	0.20
Tocopherol acetate	0.50
Water	10.00
Glycerin	. 7.00
Niacinamide	2.00
Phenylbenzimidazole sulphonic acid	1.00
(Parsol HS)	
Triethanolamine	0,62
Panthenol	0.50

Methyl parabens	0.10
Disodium EDTA	0.10
Benzyl alcohol	0.25

In a suitable vessel, add the triethanolamine and Parsol HS to the water and all to mix using conventional technology until a clear phase is achieved. Then add the water, glycerine, niacinamide, panthenol, methyl parabens, disodium EDTA and benzyl alcohol. They are mixed using the same system until a clear phase is achieved.

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In a separate vessel, pre-disperse the iron and titanium dioxides, propyl parabens, ethyl parabens and KSG21 in the cyclomethicone (DC245) and Permethyl with high shear mixing e.g., Standard Silverson assembly at 8,000 rpm. Then add the DC9040 and tocopherol acetate and mill using a Silverson on low speed until homogeneous. In a separate vessel, warm and agitate the Butylmethoxydibenzoylmethane, Octylsalicylate and Octocrylene until a clear uniform liquid is obtained. Add this liquid to the pigment /elastomer dispersion and mix with a Silverson on low speed until homogeneous.

Then add the clear water phase to the colored phase and mill again using a Silverson at 8,000 rpm until the water is full incorporated and an emulsion is formed. Then incorporate into the appropriate package.

Examples IX - X

Cream foundations are made that are suitable for application to the face to provide softening, moisturization and conditioning and effective reduction in the appearance of oily/shiny skin.

Ingredient	<u>IX</u>	<u>X</u>
Cyclomethicone	31.00	31.00
DC9040 Silicone Elastomer Gel	17.50	17.50
Ethylene/Acrylic Acid Copolymer microspheres (Flobeads EA	10.00	10.00
209 supplied by Kobo Products Inc.)		
Emulsifying elastomer gel (KSG 21)	5	5
Silica and Titanium Dioxide and Iron Oxides (Ronasphere LDP)	10.00	-
Allyl methacrylates copolymer (Polypore L200)	2.00	2.00
Magnesium Aluminum Silicate (Sebumase)	-	5.00
Silica	-	5.00

Dimethicone Copolyol (Abil EM90)	0.5	0.5
Water	15.00	15.00
Glycerine	10.00	10.00
Niacinamide	3.50	3.50
Preservative	0.50	0.50
Total	100.00	100.00

In a suitable vessel, mix the cyclomethicone and Abil EM90, and mix under high shear to disperse the polymer. Mix together the water compatible materials in a separate vessel and mix until clear. Emulsify the mixture by mixing under high shear. Add the Silicone elastomer gel and mix to homogeneity. Add the remainder of the materials and mix until homogeneous.

Examples XI - XIII

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Cream foundations are made that are suitable for application to the face to provide a long-lasting, softening, moisturization and conditioning effect and reduce the appearance of oily/shiny skin.

	Phase	IX	XII	XIII
Ingredient		Wt%	Wt%	Wt%
Non-emulsifying elastomer			25	30
gel (DC9040)	Α	40		; ;
Cyclopentasiloxane	A	20	34	14
Emulsifying elastomer gel			5	5
(KSG21)	Α	5		
Particulates				
Allyl methacrylates		-	-	1.5
crosspolymer				
Treated powders*		11	12	12.5
Film forming agents				
Polysilicone 7 (silicones		-	-	17
plus polymer SA70)				
Solidifying agents				
Stearyl Dimethicone		-	3	-
Water Phase				

Deionized Water	9	10	16
Glycerin	10	10	3
Preservatives	1	1	1
Sunscreens	4	-	-

^{* =} mixture of iron oxides and titanium dioxides

In a suitable stainless steel vessel, mix the phase A ingredients until homogeneous. In a separate vessel equipped with a heat source, heat the water phase materials to 50°C and mix until homogeneous. Add the sunscreen materials, preservatives, film formers and particulates to the batch and mix to homogeneity. If using solidifying agents, heat the cyclopentasiloxane mixture to a temperature required to melt the solidifying agents and add the solidifying agents.

Cool both the water phase and silicone phase to below 30C and mix under high shear to form an emulsion.

Examples XIV-XV

Liquid foundations of the present invention are made as follows.

XIV

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Phase	<u>Ingredient</u>	<u>Wt %</u>
A	X-21-5507	12.50
A	KSG-15	37.50
A	Propyl paraben	0.20
A	Isononyl Isononanoate	7.00
Α	SAT-TR-77891	8.97
A	DHL-Y-77492	0.86
A	DHL-R-77491	0.12
A	DHL-B-77499	0.05
В	Methyl Paraben	0.12
В	Polyderm PE/PA	13.00
В	Glycerine	6.07
В	AMP95	0.14
В	SMO	0.60
В	Water	12.87
	· .	100.00

<u>xv</u>

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Phase	Ingredient	Wt %
A	KSG-15	33.00
A	KSG-21	11.00
A	Isononyl Isononanoate	6.16
В	GLW75AMPC (74.75% TiO2, 12.5% Water, 12.5%	10.55
	Glycerin, 0.25% AMP)	
В	GLW45YAMP (45% Fe2O3, 28.46% Water,	1.68
	26.30% Glycerin, 0.24% AMP)	
В	GLW55RAMP (55% Fe2O3, 23.25% Water,	0.20
	21.50% Glycerin, 0.25% AMP)	
В	GLW60BAMP (60% Fe2O3, 21.67% Water,	0.08
	19.80% Glycerin, 0.25% AMP)	
В	Polyderm PE/PA	12.10
В	AMP95	0.09
В	Glycerine	3.53
В	Water	21.08
В	SMO (O-1570 Ryoto Sugar Ester)	0.53
	Total	100.00

Combine each of the ingredients in the that that contains the pigments and mix at 5000 RPM for 30 minutes or until ingredients are dispersed. Combine each of the ingredients in the non-pigment containing phase and mix at a maximum of 1300 rpm until homogeneous (for about 10-15 minutes). Slowly add the water phase to the silicone phase until emulsion is properly mixed. Once mixed, pour mixture into proper container and store for use.

Examples XVI - XX

10 Liquid foundations are made as follows:

Ingredient	Phase	Wt%	Wt%	Wt%	Wt%	Wt%
Cyclopentasiloxane	A	21.64	33.64	18.14	12.75	14.30
DC9040 Silicone Elastomer Gel	A	40.00	25.00	40.00	30.00	30.00
KSG-21 Elastomer Gel	A	5.00	5.00	5.00	5.00	5.00
Polysilicone-7	В	0.00	0.00	0.00	17.39	17.39
Allyl Methacrylates	В	0.00	0.00	0.00	1.50	1.50
Crosspolymer						
Stearyl Dimethicone		0.00	3.00	0.00	0.00	0.00

Titanium Dioxide & Mineral Oil	A	9.90	9.90	9.90	9.90	0.00
& Methicone						
Titanium Dioxide and	A	0.00	0.00	0.00	0.00	8.25
Triethylcaprylsilane		ļ				
Preservatives	В	0.30	0.30	0.30	0.30	0.30
Pigments	A	3.16	3.16	3.16	3.16	3.26
Butyl Methoxydibenzoylmethane	В	0.00	0.00	1.00	0.00	0.00
Octyl Salicylate	В	0.00	0.00	2.00	0.00	0.00
Octocrylene	В	0.00	0.00	0.50	0.00	0.00
Water	-	9.55	9.55	8.33	16.55	16.55
Phenylbenzimidazole Sulphonic		0.00	0.00	0.60	0.00	0.00
Triethanolamine		0.00	0.00	0.62	0.00	0.00
Glycerin		10.00	10.00	10.00	3.00	3.00
Methyl Paraben		0.10	0.10	0.10	0.10	0.10
Disodium EDTA		0.10	0.10	0.10	0.10	0.10
Benzyl Alcohol		0.25	0.25	0.25	0.25	0.25

In a suitable stainless steel vessel, mix the phase A ingredients until homogeneous. In a separate vessel equipped with a heat source, heat the water phase materials to 50°C and mix until homogeneous. Add the sunscreen materials, preservatives, film formers and particulates (phase B) to the batch and mix to homogeneity. If using solidifying agents, heat the cyclopentasiloxane mixture to a temperature required to melt the solidifying agents and add the solidifying agents. Cool both the water phase and silicone phase to below 30C and mix under high shear to form an emulsion.

methacrylate powder, polystyrene powder, silk powder, crystalline cellulose, starch, titanated mica, iron oxide titanated mica, bismuth oxychloride, pearl, pearl mica, interference pigments and mixtures thereof.

- 9. The cosmetic composition of Claim 1 in the form of a foundation, mascara, concealer, eyeliner, brow color, eye shadow, blusher, lip paint or lipstick.
- 10. The cosmetic composition of Claim 1 wherein said composition further comprises an active selected from the group consisting of a sunscreen active, a film forming agent, a shine control agent, and combinations thereof.

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(54) Title: COSMETIC COMPOSITIONS

(57) Abstract: The invention relates to cosmetic compositions comprising a combination of non-emulsifying and emulsifying crosslinked siloxane elastomers.

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A61K7/48 COSL C08L83/00 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 A61K Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to dalm No. Citation of document, with indication, where appropriate, of the relevant passages Category * 1-10 EP 0 295 886 A (TORAY SILICONE) A 21 December 1988 (1988-12-21) claims 1-4; table 4 FR 2 768 926 A (L'ORÉAL) 1-10 Α 2 April 1999 (1999-04-02) claims 1-29; example 2 1-10 EP 1 097 968 A (DOW CORNING) P,X 9 May 2001 (2001-05-09) claims 1-8 1-10 EP 1 062 944 A (SHINETSU) Ρ, Χ 27 December 2000 (2000-12-27) claims 1-28; example 12 -/--Patent family members are listed in annex. Further documents are listed in the continuation of box C. Special categories of cited documents: T later document published after the International Ming date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the *A* document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another challon or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled "O" document referring to an oral disclosure, use, exhibition or other means in the art. document published prior to the international filing date but later than the priority date claimed '&' document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 25/07/2002 15 July 2002 Authorized officer Name and mailing address of the ISA European Patent Office; P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 Willekens, G

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